Pyridinium tetrakis(nitrato-$\kappa^2 O,O'$)-(2,2′:6′,2″-terpyridine-$\kappa^3 N$)cerate(III) pyridine solvate and bis(methanol-κO)tris(nitrato-$\kappa^2 O,O'$)(2,2′:6′,2″-terpyridine-$\kappa^3 N$)cerium(III)

Mikhail S. Grigoriev,[a]* Christophe Den Auwer[b] and Charles Madic[c]

[a]Institute of Physical Chemistry, Russian Academy of Sciences, 31 Leninsky Prospekt, 119991 Moscow, Russia, [b]CEA/VALRHO Marcoule, DEN/DRCP/SCPS/LCAM, Bâtiment 166, BP 171, 30207 Bagnols-sur-Cèze CEDEX, France, and [c]CEA/Saclay, DEN/DIR, Bâtiment 450, 91191 Gif-sur-Yvette CEDEX, France
Correspondence e-mail: grigoriev@ipc.rssi.ru

The title complexes, $(C_5H_6N)[Ce(NO_3)_4(C_{15}H_{11}N_3)]\cdot C_5H_5N$ or $(Hpy)[Ce(NO_3)_4(terpy)]\cdot py$, (I) (py is pyridine, C_5H_5N, and terpy is terpyridine, $C_{15}H_{11}N_3$), and $[Ce(NO_3)_3(C_{15}H_{11}N_3)(CH_4O)_2]$ or $[Ce(NO_3)_3(terpy)(OHCH_3)_2]$, (II), are 11-coordinate. The coordination polyhedron of the Ce atom in (I) is irregular, while that in (II) can be described as an icosahedron with two vertices replaced by one.

Comment

The terpyridine ligand (terpy) and its derivatives are promising candidates for the liquid–liquid extraction and separation of metal ions, especially in the reprocessing of spent nuclear fuel (Chan *et al.*, 1996; Byers *et al.*, 1996). Structural characterization of these complexes in the solid state is of particular importance for understanding the extraction processes. As usually happens, the nitrate-containing complexes, which exhibit higher coordination numbers, are rather difficult subjects for the analysis of coordination polyhedra. The highest coordination number of 11 was found in two lanthanide complexes with terpyridine, $H_2terpy[Sm(NO_3)_4(terpy)]NO_3$ (Drew *et al.*, 1998) and [La-$(NO_3)_2(terpy)_2][La(NO_3)_4(terpy)]$ (Fréchette & Bensimon, 1995). However, the coordination polyhedra of the lanthanide atoms were not discussed in these two publications. In publications devoted to the systematic analysis of coordination polyhedra, coordination number 11 is also usually omitted from consideration (Bombieri & De Paoli, 1985; Favas & Kepert, 1981; Kepert, 1982). Here, we present two further structures of 11-coordinate lanthanide complexes with terpyridine, namely (Hpy)[Ce(NO_3)_4(terpy)]·py, (I), and [Ce-$(NO_3)_3(terpy)(OHCH_3)_2]$, (II).

The complex anion $[Ce(NO_3)_4(terpy)]^-$ (Fig. 1) in (I) contains a tridentate terpyridine ligand and four bidentate nitrate groups. The distance from the Ce atom to the least-squares plane of the terpyridine ligand is 0.492 (2) Å. The

(I)

(II)
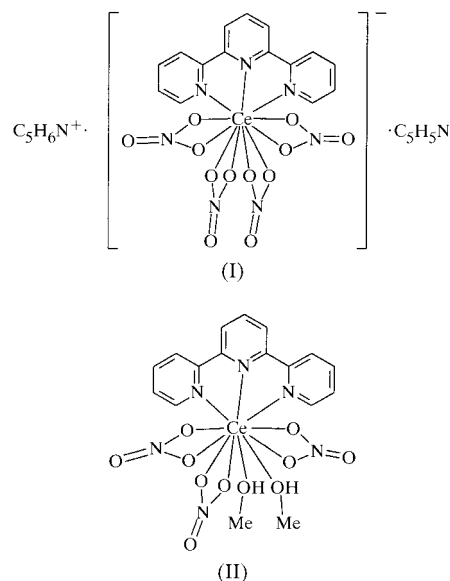
Ce—N distances are 2.624 (2), 2.706 (2) and 2.625 (2) Å for N1, N12 and N18, respectively. The Ce—O distances to the eight O atoms of the nitrate groups vary from 2.570 (2) to 2.709 (2) Å. One of the two pyridine solvate molecules is protonated, compensating for the charge of the anion, and it forms a hydrogen bond with the other, uncharged, pyridine molecule [N6···N7 2.652 (5) Å]. In the framework of the space group $P2_1/c$, the H atom is disordered between the two N atoms of the pyridine molecules.
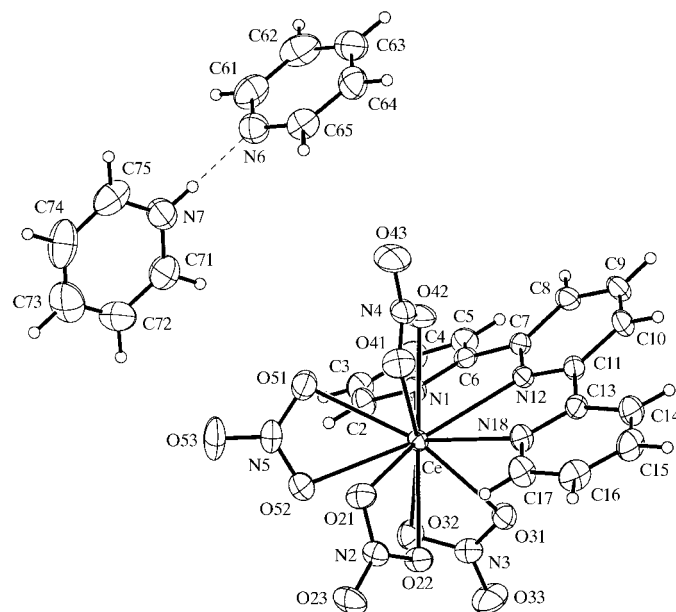

Figure 1
The molecular structure of (I) showing 30% probability displacement ellipsoids. H atoms are represented as spheres of arbitrary radii. Only one position of the disordered H atom is shown.

metal-organic compounds

The molecular complex (II) (Fig. 2) contains a tridentate terpyridine ligand, three bidentate nitrate groups and two coordinated methanol molecules. The distance from the Ce atom to the least-squares plane of the terpyridine ligand is 0.760 (2) Å. The Ce—N distances are 2.682 (2), 2.685 (2) and 2.705 (2) Å for N1, N12 and N18, respectively. The Ce—O distances to five of the O atoms of the nitrate groups vary from 2.537 (2) to 2.712 (2) Å, whereas the distance for the sixth atom is 2.942 (3) Å. The coordinated MeOH molecules form hydrogen bonds (Table 1) with one coordinated and one non-coordinated O atom of two different nitrate groups of other complexes.
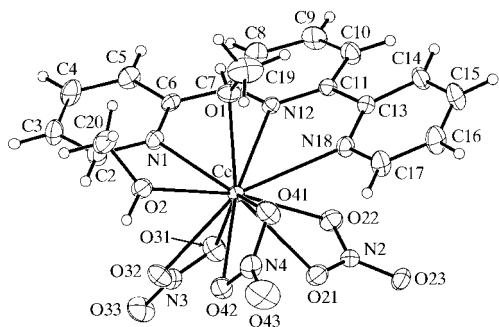

Figure 2
The molecular structure of (II) showing 30% probability displacement ellipsoids. H atoms are represented as spheres of arbitrary radii.

It has recently been found, for complexes containing ter-pyridine ligands (Drew *et al.*, 1999), that when the average M—N distance to the terpy ligand is longer than 2.58 Å, the central M—N bond is longer than the others. The Ce—N distances in (I) are in a good agreement with this observation, while in (II), all three distances are almost equal. In our opinion, this shows the significance of the effect of the different ligand arrangement on bond lengths.

The significant elongation of one Ce—$O_{nitrate}$ bond in (II) is a consequence of the change of the coordination sphere, resulting in the lower stability of the high coordination number; one bidentate nitrate ligand with a small bite distance has been replaced by two monodentate ligands.

The coordination polyhedron of the Ce atom in (I) (Fig. 3) is irregular and difficult to describe, whereas that in (II) can be described as an icosahedron with one missing vertex or, more exactly, with two vertices replaced by one (the only vertex sharing six edges). It is interesting to note that the coordination polyhedron of the Sm atom in H$_2$terpy[Sm(NO$_3$)$_4$-(terpy)]NO$_3$ (Drew *et al.*, 1998) (Fig. 3), and that of the 11-coordinate La atom in [La(NO$_3$)$_2$(terpy)$_2$][La(NO$_3$)$_4$(terpy)] (Fréchette & Bensimon, 1995), can be described in the same way and the positions of the terpyridine ligand and the three nitrate anions are the same as in (II); the fourth nitrate anion occupies the place of two methanol molecules. This shows that the origin of the difference between the coordination polyhedra in (I) and (II) does not lie in the charge difference between the complexes.

One further example of coordination number 11 can be found in the Ce^{IV} complex with a structural analogue of ter-pyridine, [Ce(NO$_3$)$_4$L], where L is 2,4,6-tri-*tert*-butylpyridyl-1,3,5-triazine (Chan *et al.*, 1996). In this case, the coordination polyhedron is also similar to that found in (II) (if we consider two neighbouring triangular faces with a dihedral angle of 1.9° to be two separate faces), but the arrangement of the ligands is different.
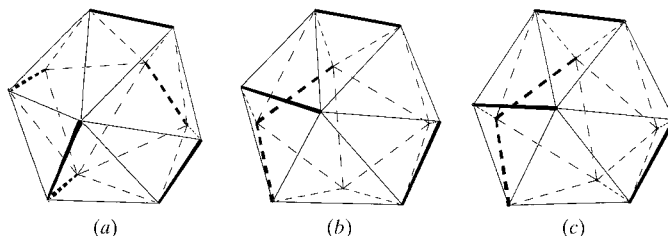

Figure 3
The coordination polyhedra of the Ln atoms in (*a*) (I), (*b*) (II) and (*c*) (H$_2$terpy)[Sm(NO$_3$)$_4$(terpy)]NO$_3$ (Drew *et al.*, 1998). The positions of the terpy and nitrate groups are shown with heavy lines.

In general, the present study has demonstrated a surprising stability of the geometry of the coordination sphere for complexes with coordination number 11.

Experimental

For the synthesis of (I), acetonitrile (0.5 ml) was added to a mixture of Ce(NO$_3$)$_3$·6H$_2$O (0.2 mM) and terpy (0.2 mM). After 1 d, pyridine (1.5 ml) was added. Crystals of (I) were obtained after slow evaporation of the solution at 293 K. Crystals of (II) were obtained by slow diffusion of solutions of Ce(NO$_3$)$_3$·6H$_2$O and terpy in methanol through pure methanol in a U-shaped glass tube at 293 K.

Compound (I)

Crystal data

(C$_5$H$_6$N)[Ce(NO$_3$)$_4$(C$_{15}$H$_{11}$N$_3$)]·-C$_5$H$_5$N	D_x = 1.732 Mg m^{-3}
M_r = 780.64	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 23 126
a = 13.0982 (3) Å	reflections
b = 12.8311 (3) Å	θ = 1.6–27.5°
c = 17.8255 (3) Å	μ = 1.60 mm^{-1}
β = 91.6958 (12)°	T = 293 (2) K
V = 2994.52 (11) Å^3	Prism, yellow
Z = 4	0.2 × 0.2 × 0.2 mm

Data collection

Nonius KappaCCD area-detector diffractometer	23 126 measured reflections
	6770 independent reflections
φ and ω scans to cover a hemisphere of reciprocal space	5416 reflections with $I > 2\sigma(I)$
	R_{int} = 0.099
Absorption correction: empirical (*MULABS* in *PLATON*; Spek, 1998)	θ_{max} = 27.5°
	h = −15 → 17
	k = −15 → 16
T_{min} = 0.673, T_{max} = 0.702	l = −21 → 23

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.082$
$S = 1.05$
6748 reflections
424 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0355P)^2 + 0.349P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 1.23$ e Å^{-3}
(1.34 Å from Ce)
$\Delta\rho_{min} = -2.87$ e Å^{-3}
(0.04 Å from Ce)

Compound (II)

Crystal data

$[Ce(NO_3)_3(C_{15}H_{11}N_3)(CH_4O)_2]$
$M_r = 623.50$
Triclinic, $P\bar{1}$
$a = 7.7460$ (2) Å
$b = 12.2280$ (3) Å
$c = 12.3405$ (3) Å
$\alpha = 91.253$ (2)°
$\beta = 103.238$ (2)°
$\gamma = 96.510$ (2)°
$V = 1129.09$ (5) Å^3

$Z = 2$
$D_x = 1.834$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9758 reflections
$\theta = 1.7–26.3°$
$\mu = 2.09$ mm^{-1}
$T = 293$ (2) K
Plate, yellow
$0.30 \times 0.25 \times 0.10$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans to cover a hemisphere of reciprocal space
Absorption correction: empirical (*MULABS* in *PLATON*; Spek, 1998)
$T_{min} = 0.47$, $T_{max} = 0.78$

9758 measured reflections
4502 independent reflections
4278 reflections with $I > 2\sigma(I)$
$R_{int} = 0.062$
$\theta_{max} = 26.3°$
$h = -9 \rightarrow 9$
$k = -15 \rightarrow 15$
$l = -15 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.087$
$S = 1.02$
4495 reflections
326 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0554P)^2 + 0.1P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.04$ e Å^{-3}
(1.04 Å from Ce)
$\Delta\rho_{min} = -1.75$ e Å^{-3}
(0.86 Å from Ce)

Table 1
Hydrogen-bonding geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$\cdots$O23^i	0.80 (4)	1.96 (5)	2.750 (3)	172 (4)
O2—H2$\cdots$O32^{ii}	0.88 (5)	1.92 (5)	2.775 (3)	165 (4)

Symmetry codes: (i) $1 + x, y, z$; (ii) $1 - x, 1 - y, 1 - z$.

The H atoms bonded to the C atoms of the terpy ligands and pyridine solvate molecules (including the protonated one) were introduced in calculated positions (C—H = 0.93 Å), with displacement parameters fixed at 1.2 times those of the atom to which they were bonded. The position of the protonated N atom in (I) is disordered between the two pyridine molecules (occupancy 0.50:0.50). The H atoms of the OH groups of the methanol molecules in (II) were located from a difference Fourier map and refined with individual isotropic displacement parameters. The orientation of the CH$_3$ groups of the methanol molecules in (II) was found from a difference Fourier map and refined. The H atoms of the CH$_3$ groups were introduced in calculated positions (C—H = 0.96 Å), with displacement parameters fixed at 1.5 times those of the parent C atom.

For both compounds, data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL* (Otwinowski & Minor, 1997); data reduction: *HKL*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *SHELXTL* (Sheldrick, 1997); software used to prepare material for publication: *SHELXTL*.

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